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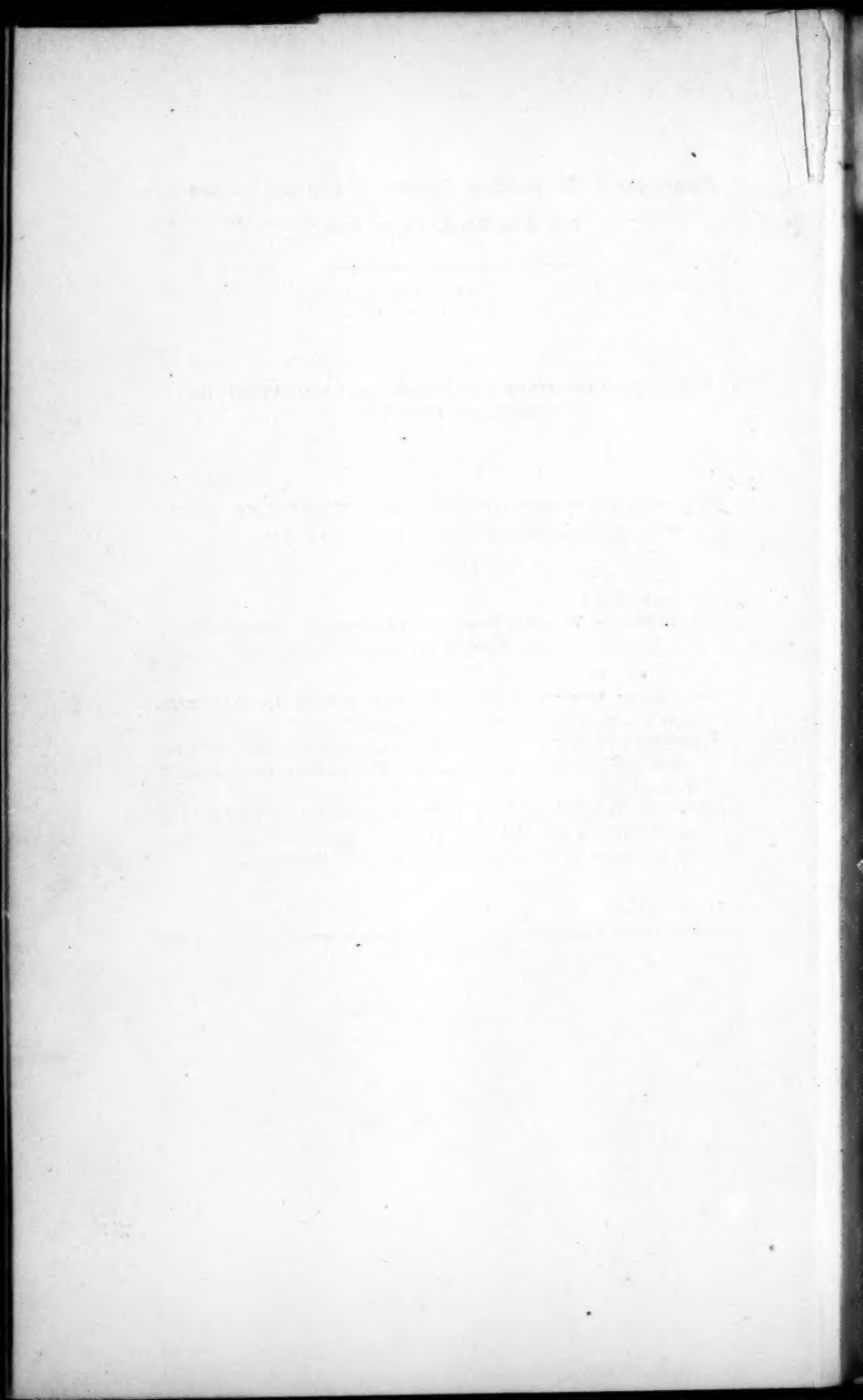
CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

*THE ELIMINATION OF THERMOMETRIC LAG AND
ACCIDENTAL LOSS OF HEAT IN
CALORIMETRY.*

BY THEODORE WILLIAM RICHARDS, LAWRENCE J. HENDERSON,
AND GEORGE S. FORBES.

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2. *THE CONSTANCY OF RESULTS OBTAINED BY ONE OF THE NEW METHODS.* — BY THEODORE W. RICHARDS AND GEORGE S. FORBES.
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1. TWO NEW METHODS OF AVOIDING ERROR IN CALORIMETRY.

By THEODORE W. RICHARDS.

It is very well known that the error most difficult to overcome in calorimetric work is the accidental exchange of heat with the environment by radiation, convection, and conduction. Very few calorimetric results are wholly free from error due to this cause, even comparative methods, like that of Pfaundler,* being dependent upon the assumption that the loss of heat in two similar sets of apparatus are equal, one to the other. Thermo-chemical results, especially those involving deliberate reactions, are notoriously subject to uncertainty on account of the magnitude of their corrections for cooling. The effort to annihilate such error as this was the guiding thought in a preceding investigation of

* Sitzungsber. d. Akad. Wiss. Wien, 62-2, 379 (1870).

Richards and Lamb,* and the present paper is written to elaborate the argument there presented, as well as to suggest new methods of overcoming the difficulty.

An analysis of the sources of uncertainty due to this cooling effect in a reaction evolving heat easily reveals two chief factors: first, the deficiency of the actual maximum temperature in the calorimeter due to loss of heat, and, secondly, the inability of the thermometer to follow with adequate speed the actual temperature. The first of these causes of error receives a more or less satisfactory elimination by the methods of Regnault and Rumford; the second seems never to have been adequately treated.

First, the former question may be briefly discussed. The method of Regnault as formulated by Pfaundler depends upon Newton's law of cooling, which is known to hold with reasonable accuracy for small temperature intervals.† It must be noted, however, that this application of Newton's law is not wholly free from assumption; for the law has been tested only during long-continued cooling, not when the temperature is subject to rapid change. In this latter case it seemed quite possible that the convection currents, to which the cooling is partly due, are not at once started in full activity; and hence that the rate of cooling after a sudden change of temperature is not identical with that during a slow change.

Rumford's method of correction is subject to a somewhat similar possible uncertainty of unknown magnitude, and this method (of starting a reaction as much below the temperature of the room as the reaction finishes above the temperature of the room) is moreover only applicable to reactions which progress evenly throughout their course. The consideration of these circumstances led to a wish to devise a method free from the objections to which these corrections for cooling are open; and this wish was intensified by the consideration of the second of the causes of error already alluded to,—namely, the lag of the thermometer.

Although this latter cause of error is not usually considered in the treatment of calorimetric work, it necessarily enters to a greater or less extent into all results in which the temperature is read on a moving thread.

The rate of cooling of the mercury in the thermometer, and therefore the lag of its reading, varies very greatly with the construction, form, and size of the thermometer, and also with the specific heat, conductivity, and agitation of the surrounding liquid. Therefore it must be determined for each thermometer under the exact conditions employed in each case.

* These Proceedings, 40, 657 (1905).

† Pogg. Ann., 129, 113 (1866).

Nevertheless, it may be of interest to record two typical tests of a Beckmann thermometer, such as is usually furnished by Fuess or Goetze, because this type of thermometer is now so much used for calorimetric work.

The lag was determined very simply by plunging the slightly warmed thermometer into a large flask full of water at the temperature of the room, which was itself maintained at a constant point by a thermostat attachment to the steam-heating coil. The change of reading of the thermometer with time was then recorded. During the time of an experiment the bath did not vary in temperature by an appreciable amount. Two series of experiments were made at different times,—one in which the thermometer was clamped and the liquid was not stirred, and the other in which the liquid was stirred by means of the thermometer itself. The lag was of course much greater in the former case than in the latter. Below are given the data and corresponding curves of two experiments typical respectively of these two series, and representing a fair average of their somewhat irregular results.

LAG OF BECKMANN THERMOMETER UNDER DIFFERENT CONDITIONS.

Time Seconds.	Curve A.		Curve B.	
	Reading when not Stirred.	Lag.	Reading when Stirred by Thermometer.	Lag.
0	6.00	...	6.00	...
15	3.450	0.053°
30	3.428	0.031°
45	3.410	0.013°
60	3.36	0.049°	3.401	0.004°
75	3.345	0.034°	3.3985	0.0015°
90	3.335	0.024°	3.397	0.000°
120	3.324	0.013°	3.397	0.000°
180	3.314	0.003°	3.397	0.000°
240	3.312	0.001°
300	3.311	0.000°
360	3.311	0.000°

Curves *A* and *B* given in the above table are plotted in the diagram, which explains itself.

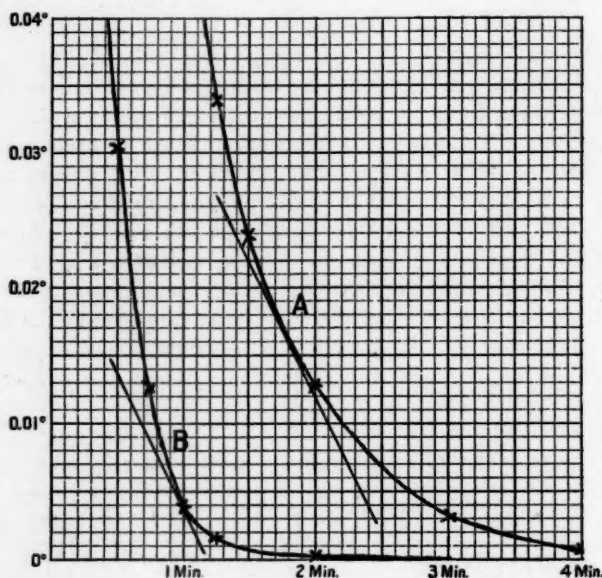


FIGURE 1.

The application of these results to a calorimetric experiment is very simple. Obviously, the thermometer will always lag as much behind the temperature of a given bath of changing temperature as it was behind the bath at the time when its own temperature was changing at the same rate as that of the bath. Because the tangent of a curve at any point indicates the direction of the curve at that point, the lag is simply found by determining the point at which a line drawn at the required angle just touches the curve. For example, if the bath were cooling 0.020° per minute, the ordinate of the point of contact of the curve with a tangent drawn at the corresponding angle (0.02° per minute) in the diagram will give at once the lag. Thus in the case of the present thermometer, the lag would be 0.017° (Curve A) if the liquid were not stirred, and 0.004° (curve B) if it were stirred, as indicated by the tangents drawn on the diagram. Even in the most favorable case, the correction would probably amount to over 0.001° , and should therefore always receive consideration.

As has been said, each experimenter must of course determine this value for his own exact conditions; therefore it is impossible here to apply a suitable correction to previous investigations, although all must have been more or less affected by this cause of error. The Rumford method of eliminating the error from radiation is little better than the Regnault method in this respect; for the rising thermometer just before the beginning of the reaction will always give too low a reading, while the conditions at the close of the reaction are highly uncertain.

On account of this phenomenon of thermometric lag, and because of the uncertain application of Newton's law of cooling to systems suffering sudden changes of temperature, it seemed highly desirable to devise a method of wholly eliminating both irregularities. It appeared probable that this object might be accomplished by artificially changing the temperature of the environment of a reacting system at the same rate as the system itself changed in temperature.* Thus a given reaction might be made really adiabatic, neither losing nor gaining heat from its equally hot surroundings at any time during the reaction.

Obviously there are several ways in which the outside water jacket in a calorimeter might be heated in order to accomplish this purpose. The simple device of pouring in hot water might be employed, or the water might be warmed by an electrically heated resistance coil, or the jacket itself might be made the scene of a chemical reaction of the same speed and thermal intensity as that within the calorimeter itself.

Of these and other methods which suggested themselves the last named seemed the most convenient and suitable for a chemical laboratory. It has the special advantages that before the beginning of operations all the apparatus and material employed may be at the temperature of the room; that the maximum temperature attained may be easily calculated with great nicety; that no point in the system can ever exceed this maximum temperature, if the reaction is suitably chosen; and that the speed of the reaction may be simply regulated by a stop-cock admitting one of the reacting substances.

The following sections of this paper show how this suggestion has already proved serviceable in two important investigations in this laboratory, and serve to give an approximate idea of the conditions necessary for its satisfactory fulfilment.

* After the present paper had gone to press it was found that S. W. Holman had suggested this, although without in any way testing the suggestion in practice. These Proceedings, 31, 252 (1895).

2. THE CONSTANCY OF RESULTS OBTAINED BY ONE OF THE NEW METHODS.

BY THEODORE W. RICHARDS AND GEORGE S. FORBES.

The experiments whose description follows in this section show how, in cases of comparative calorimetry, measurements can be conducted by heating the environment with constancy greater than that attainable with the same apparatus by the use of a cooling correction. It will also be shown that further study and improvement of the method may render possible the direct determination of the true adiabatic rise of temperature in any calorimetric process.

In the course of a certain investigation, to be described later in detail, it became desirable to compare the heat capacities of mercury and of liquid amalgams of zinc and cadmium. It is not necessary to describe the apparatus in great detail here. A sheet-iron calorimeter containing eleven hundred grams of toluol was supported in the center of a tinned iron vessel, which was immersed in a large bath of water contained in a galvanized-iron barrel. An annular cover protected the air space around the calorimeter from disturbance. Twenty-three hundred grams of mercury were delivered from a warm reservoir of very constant temperature and distributed into a series of shallow pans; all of these were insulated from the walls of the calorimeter by the toluol, which was kept in rapid circulation by a complicated and efficient stirrer. The warming effect due to the agitation of the liquid was considerable, but very constant. The maximum temperature was always attained within four minutes, and was read by a Beckmann thermometer graduated to hundredths; an electric buzzer prevented errors due to the friction of the thread. The thermometer was not calibrated, but the same part of its scale was used in every experiment. After the apparatus was in running order, and the details of its manipulation mastered, a series of determinations of the heat capacity of mercury, in certain arbitrary units, was made. The indications of the thermometer were carefully noted, and interpreted in the usual way, applying the usual Regnault-Pfaundler method for correcting the error from radiation.*

Four successive determinations of the heat capacity of mercury in these arbitrary units were 608, 613, 614, 607, average 611 ± 1 .

The probability is that this mean value represents approximately the mean of an indefinite number of results by this process, but never-

* Pfaundler, Pogg. Ann., 129, 113 (1866).

theless the considerable deviation between the extreme values is greater than we can easily ascribe to uncertainty in the reading of a thermometer, or inaccuracy of weighing. Hence it appeared that the cooling correction, which here amounted to about 5 per cent of the rise of temperature, was probably at fault.

A series of determinations was next made with the same apparatus, increasing the temperature of the surrounding jacket at the same rate as that of the calorimeter. To accomplish this, a suitable weight of sodic hydroxide was dissolved in the jacket, and just at the instant when the mercury was delivered from its reservoir an equivalent mass of sulphuric acid was poured into the caustic solution from four different outlets, so placed as to make the initial distribution of the acid as uniform as possible. A powerful stirrer completed the mixing within a short time, as was proved by the indications of a thermometer hung in the reacting mixture. The total rise of the bath under these circumstances was almost exactly the same as that observed in the calorimeter, and ran nearly parallel to it; hence radiation from the sides and bottom of the calorimeter must have been minimized if the influence of the adjacent body of air is negligible. The partial exposure of the top of the liquid still left a slight cooling effect, which had to be corrected arithmetically; but this could easily have been avoided in more elaborate experiments.

Three determinations made in this way gave the results 605, 606, 608, average 606 ± 0.06 , thus possessing a smaller probable error than any three determinations chosen from among the previous series. Such irregularity as exists was probably due to the fact that the bath was not exactly regulated to the proper rate of temperature increase. The result is also distinctly lower than the preceding series, showing that the temperature interval had previously been estimated as too large. The difference of 0.8 per cent in the averages of the two series is a very important one. Possibly the value 606 may have been slightly too low, owing to the large air-space between the calorimeter and jacket, but it could hardly have been as much too low as 0.8 per cent.

In order to obtain further light upon the matter, another series of determinations was made, in which the environment was warmed in such a way as certainly to yield too high a result. The acid and alkali in the jacket of the calorimeter were mixed exactly two minutes before the hot mercury was run into the calorimeter itself, and the final temperature of the environment was made high enough to counterbalance the slight cooling effect on top. Therefore during the first two minutes there was undoubtedly an excessive warming effect. The results thus found were

610, 613, 611, 612; average 611.5 ± 00.4 , or almost exactly identical with value 611 of the first series calculated by Regnault's method. Because, however, the results of this last series must certainly have been too high, the results calculated by Regnault's method must also be too high; and it is clear that one cause, if not the only cause, of this error must be the lag of the thermometer.

It is to be noted that in the last series, where irregular radiation-effects took place only during two minutes, the results are more concordant with one another than in the first series, where the total period of irregular radiation was fifteen minutes. This fact again indicates that the calculated cooling correction was at fault.

On studying these figures, it is clear that where only comparative results are required, the method of heating the environment will give satisfactory results so long as the conditions in every experiment are identical. Even when the environment is warmed two minutes too soon, the results are constant; but of course if this procedure is adopted once in a series, it must be always adopted.

Therefore, even if the method of warming the environment were incapable of yielding an absolute value, it would nevertheless be a distinct addition to comparative calorimetry. In the following section it will be shown that under proper precautions the method will probably yield not only a constant value, but a result very close to the true value.

3. THE COMPARISON OF THE TWO METHODS, AND THE EXACT ESTIMATION OF ADIABATIC RISE OF TEMPERATURE.

BY THEODORE W. RICHARDS AND L. J. HENDERSON.

The foregoing sections of this paper show indubitably that whenever there is any considerable rate of cooling in a calorimetric experiment, the lag of the thermometer will cause the result to be higher than the truth.

It becomes now a matter of great interest to determine, if possible, the method of procedure which is capable of yielding the true value for the temperature increment in a strictly adiabatic reaction. The question assumed especial importance because of an extended series of measurements of heats of combustion now in progress here. In order to procure further light, it was decided to execute several series of experiments in which the cooling correction was calculated in the usual way, and to correct these results further for the lag of the thermometer. Subsequently, the outcome of these experiments was to be compared with that of a

series in which the temperature of the environment was changed simultaneously with that of the calorimeter itself. The accomplishment of this program and the comparison of the results is recorded below.

The reaction chosen to be measured was that of sodium hydroxide on sulphuric acid. This reaction has the advantage of easy repetition, as well as the advantage of a less considerable change of heat evolution with temperature than is the case in many reactions. In order to exclude all error from this cause, the maximum temperature was about the same in all cases. A slight excess of the alkali was used to avoid error from decomposition of carbonate.

In a preliminary series of experiments the divided beaker calorimeter used by Richards and Lamb* was at first employed; but because with this apparatus the speed of the reaction is not easily regulated, another form depending upon the same principle was employed. This form is shown in section in Figure 2.

The sodic hydroxide was contained in a large test-tube provided with two holes, one on the side above the liquid level, and the other in the middle of the bottom. The latter was closed until the moment of the reaction by a rubber stopper upon a rod running down through the axis of the tube. Before this moment arrived the test-tube was immersed in the calorimeter vessel, full of dilute acid, to the level of the alkali within. When it was desired to start the reaction, the stopper was displaced and the test-tube still further immersed, so that both holes were open under the liquid level. Screw-propeller vanes on the stopper-rod made it possible to circulate the liquid through these two holes, so that the mixing could be accomplished as quickly or as slowly as was desired. Another screw-stirrer in the calorimeter vessel itself assisted the mixing. The heat developed by the friction of the stirring was found to be barely perceptible; it was moreover identical in each case, and may therefore be wholly neglected.

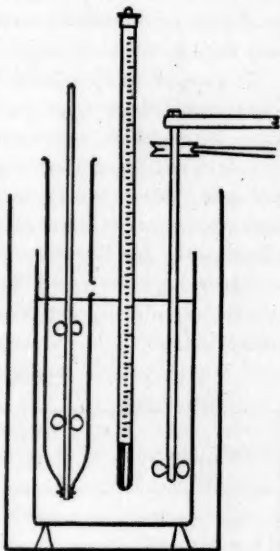


FIGURE 2.

* These Proceedings, 40, 675 (1905).

With this apparatus experiments were first made according to each of the usual methods of calorimetric work. Two distinct procedures have been used by various experimenters; in one case the experiment is started at about the temperature of the room, and a large final cooling correction is added, while in the other case the experiment is started below the temperature of the room, and a small initial correction for warming is subtracted.

In previous experiments in this laboratory it has been found that the latter of these methods gives the more constant results; and the same conclusion must have been reached by Stohmann and by Atwater, since they have usually used it.

Because of the lesser accuracy of the former of these methods, more experiments were made by it than by the latter, in order that the averages might have about equal weight.

Below are given the results of successive experiments by these two methods. The first column of the table designates the method; the second, the number of the experiments; the third, the rise in temperature as calculated by the Regnault-Pfaundler method, but not corrected for thermometric lag; the fourth, the correction for thermometric lag, as found in the way already described; and the fifth, the final value with all corrections.

PRELIMINARY EXPERIMENTS.

Method.	No. of Experiment.	Rise of Temperature as usually Calculated.	Correction for Thermometric Lag.	Final Value.	Average Rise of Temperature.
I.	12	3.382°	-0.007°	3.375°	3.3747°
	13	3.385°	-0.007°	3.378°	
	14	3.378°	-0.007°	3.371°	
II.	15	3.385°	-0.010°	3.375°	3.3777°
	16	3.388°	-0.009°	3.379°	
	17	3.386°	-0.007°	3.379°	
I.	18	3.385°	-0.007°	3.378°	3.3793°
	19	3.385°	-0.008°	3.377°	
	20	3.391°	-0.008°	3.383°	

It will be noticed that the correction for thermometric lag averages about 0.008° , or about 0.23 per cent of the total rise in temperature. This thermometric lag was not precisely similar in all the experiments, because the rate of cooling was not always exactly the same in each case.

It is further noteworthy that the two methods give essentially the same result, the average of the six determinations with the first method being $3.377^{\circ} \pm 0.001^{\circ}$, while that of the three determinations with the second method is $3.378^{\circ} \pm 0.001^{\circ}$. Thus each confirms the other.

Moreover, attention should be called to the fact that twice as many determinations were needed to secure a given degree of probability by the first method as by the second, although indeed the series are too brief to make the application of the method of least squares satisfactory.

After this comparison of the various methods of calculation formerly used, and the correction of the results for the newly applied correction for thermometric lag, it became a matter of great interest to determine whether or not the final result thus obtained is identical with that yielded in the same reaction by the new method of experimentally eliminating the correction for cooling. The results of this new comparison, even more carefully made than before, are given below.

The solutions previously used having been exhausted, new, less concentrated ones were prepared. The apparatus also was somewhat altered. A large platinum calorimeter, capable of holding over a litre, was employed to contain the reacting acid, and this was fitted into a deep copper cylinder, so as to leave an annular space of air between them only a few millimeters in thickness. It is obvious that this air jacket should be as thin as possible in order to reduce its heat capacity. The calorimeter was covered by a cardboard diaphragm, pierced with suitable holes for the thermometer, stirrer, and alkali vessel. The last was in this case not immersed in the calorimeter as before, but raised above it, with the delivery jet just touching the acid into which the alkali was to be discharged,—a change adopted in order to make the delivery as rapid as possible. The temperatures of both acid and alkali were read with great care; and because the volume and heat capacity of the latter were small, it was easy to apply a small correction for its deviation in initial temperature, that of the acid being taken as the true initial temperature. The small correction necessary is given in each case in the tables below.

The copper cylinder was highly polished inside, and was sunk deeply in a bath of water whose temperature could either be maintained at a constant point or varied at will. A second cardboard cover protected the alkali tube from accidental changes of temperature. It would of course

have been better to have a hollow cover also with provision for changing its temperature; this further improvement has since been successfully tried.

The apparatus is outlined in Figure 3, a glance at which, in connection with the foregoing description, will suffice to explain it.

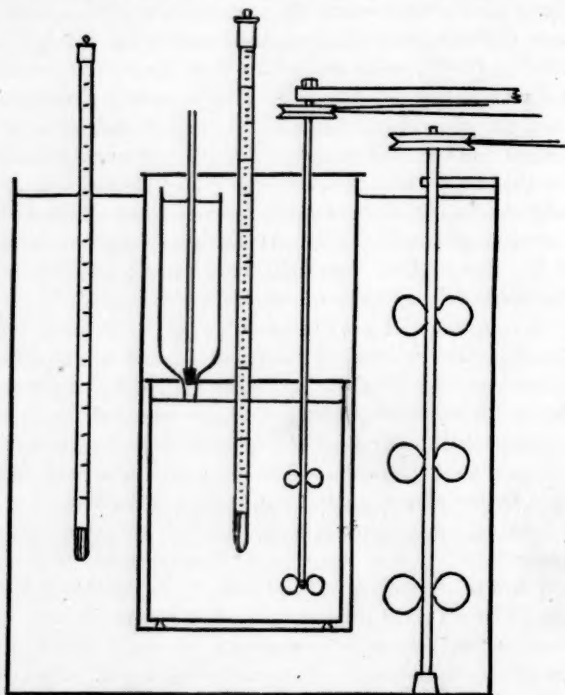


FIGURE 3.

With it, two series of determinations were made,—one, in which the temperature of the outside bath was kept constant at a temperature somewhere between the initial and final temperatures; and a second, in which the temperature of the bath was made to run parallel with the temperature of the quantitative mixture.

The first of these series is recorded in the table on the opposite page, the corrected rise of temperature being determined by the Regnault-Pfaundler formula,

$$C = nv + \frac{v' - v}{v' - \theta} + \left(\frac{\rho_n + \theta_0}{2} + \sum_1^{n-1} \theta - N\theta \right).$$

According to this formula, the reaction is divided into three periods or stages; namely, an initial period before the reaction begins, a reaction period, and a final period after the reaction is over.

In this case, $n = 5$, the number of time units (minutes) in the reaction period.

v = rate of fall of temperature in the initial period.

v' = rate of fall of temperature in calorimeter during the final period.

θ_0 = temperature at beginning of temperature rise.

$\theta_1, \theta_2, \dots$ = temperatures during successive minutes.

θ and θ' = the mean temperatures of the calorimeter during the initial and final periods respectively (easily found from θ_0 and θ_5 with the help of v and v'). All the data necessary are given in the table, including the small correction due to a deviation in the initial temperature of the alkali.

RISE OF TEMPERATURE DURING REACTION, CORRECTED IN USUAL MANNER.

	(21)	(22)	(23)	(24)	(25)
θ_0	1.950°	1.622°	1.542°	1.920°	1.968°
θ_5	4.718	4.413	4.417	4.739	4.786
$\theta_5 - \theta_0$	2.768	2.791	2.875	2.819	2.818
v	0.0036	-0.0002	-0.0068	-0.0042	-0.0140
v'	0.0184	0.0168	0.0086	0.0132	0.0126
Quantity in paren- thesis of formula)	12.6	12.7	13.0	13.0	12.6
$v' - v$	0.0148	0.0170	0.0154	0.0174	0.0266
$\theta' - \theta$	2.716	2.750	2.870	2.796	2.822
Total correction for cooling	0.087	0.077	0.036	0.061	0.049
Correction for Al- kali	+0.017	-0.005	-0.032	-0.013	0.000
Corrected rise . .	2.872°	2.863°	2.879°	2.867°	2.867°

According to the preceding evidence, the rise of temperature recorded in the last line of this table must be somewhat too high, because of the lag of the thermometer both before and after the experiment. In order to determine this amount, the lag of the thermometer was carefully studied, as on pages 5 and 6, both with a large fall of temperature and

with a small fall in temperature, under precisely the same conditions of stirring as those maintained in the foregoing experiments. In this way, consistent results were obtained, the averages of which are recorded in the curve (Figure 4).

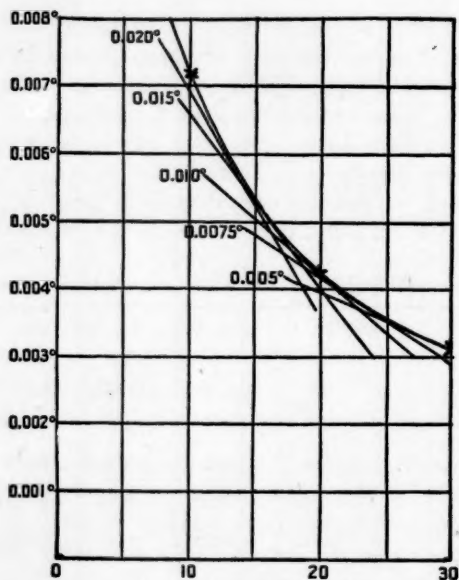


FIGURE 4.

LAG OF THERMOMETER EMPLOYED IN FOREGOING EXPERIMENTS.

The time after the immersion of the slightly warmed thermometer is recorded in the direction of abscissae in seconds; the lag of the thermometer in the direction of ordinates in 0.001° intervals. The curve represents the average of many figures. Upon it are plotted the tangents corresponding to several rates of cooling, expressed in fractions of a degree per minute. From these tangents comes the table below.

Rate of Cooling per Minute.	Lag of Thermometer.	Rate of Cooling per Minute.	Lag of Thermometer.
0.030	0.0076°	0.010	0.0042°
0.020	0.0058°	0.0075	0.0038°
0.015	0.0051°	0.0050	0.0031°

As before, the lag of the thermometer was found, both for the initial and the final readings, by drawing a tangent to the curve C at the angle determined respectively by v and v' , the rates of cooling. The results of this graphic computation are recorded in the table below.

CORRECTION OF ABOVE RESULTS FOR THERMOMETRIC LAG.

Rise of T° (Regnault- Pfaundler) in $^{\circ}\text{C}$.	Lag of Thermometer in $^{\circ}\text{C}$.			Corrected Rise of Temperature in $^{\circ}\text{C}$.
	Initial.	Final.	Total.	
2.872	-0.002	+0.006	0.004	2.868
2.863	± 0.000	+0.006	0.006	2.857
2.879	+0.004	+0.004	0.008	2.871
2.867	+0.003	+0.005	0.008	2.859
2.867	+0.001	+0.005	0.006	2.861
2.870	0.0064	2.863 $^{\circ}$

Thus the true average result is lower than that given by the Regnault-Pfaundler formula by 0.0064° , or by 0.22 per cent.

A satisfactory value having been thus found by one method, it became a matter of great interest to execute the second series by the method of warming the environment, in order to determine whether or not this would yield the same result. For this purpose the dilute acid placed in the outer jacket of the calorimeter was strongly agitated by a powerful stirrer, and at the moment of the experiment a beakerful of alkali of suitable amount was very rapidly poured into it. The temperatures inside and out were so arranged that the final temperatures were read on almost if not quite stationary thermometers, the lag of which was negligible. To accomplish this the final outside temperature had to be slightly above the final inside temperature, because of the partially unprotected top of the calorimeter. The initial and final temperatures were about the same as before, and every other condition of the experiment remained unchanged. The expression of the data is far simpler than before, it being necessary to give only the initial and final temperatures and the correction for the temperature deviation of the alkali delivered into the inner vessel; and even the latter might have been omitted if somewhat more time had been allowed it in order that it

might, before the experiment, assume the same initial temperature as the acid. The final temperature was designated θ_3 , since it was attained in three minutes.

RISE OF TEMPERATURE AS DETERMINED BY NEW EXPERIMENTAL METHOD.

	(26)	(27)	(28)	(29)	(30)
θ_0	1.658	1.665	1.851	1.503	1.798
θ_3	4.520	4.540	4.699	4.333	4.668
Correction for Alkali	0.000	-0.013	+0.012	+0.022	-0.007
$\theta_3 - \theta_0$	2.862°	2.862°	2.860°	2.852°	2.863°

The average rise of temperature as indicated by these experiments is therefore 2.860 ± 0.001 , while that obtained in the previous series after the new correction for thermometric lag had been applied was 2.863 ± 0.002 . Thus the two series, when all corrections were applied, gave results not differing by an amount greater than the sum of their probable errors, and the average by the new method had only half as large a probable error as that obtained with the old method.

While it is of course true that this agreement might have been accidental, such an interpretation to us seems improbable.

That these two methods, each of which is apparently satisfactory, should unite on the same value, gives that value a strong presumptive right to be considered as the true value. If this is so, nearly all calorimetric results which have ever been published, where any considerable rate of cooling or warming is involved, have been incorrectly calculated. In cases where the rate of cooling or warming is very slight, as in the admirable work of E. Fischer and Wrede,* the error is probably so small as to be negligible.

It is a pleasure to acknowledge our indebtedness to the Rumford Fund of the American Academy of Arts and Sciences for the apparatus used in this investigation.

SUMMARY.

1. A modification of one of the devices used by Richards and Lamb, permitting more careful regulation of the speed of reaction, is described.

* Fischer and Wrede, Sitzungsber. könig. preuss. Akad. 20, 687 (1904).

2. It is shown that the lag of the thermometer behind the temperature of even a slightly cooling or warming environment causes an appreciable error in estimating the temperature of the environment.

3. It is further shown that this lag may be easily determined and a suitable correction applied.

4. A new method for entirely obviating this and all other corrections for cooling in calorimetric work is shown to consist in systematically altering the temperature of the environment at the same rate and to the same degree as that of the calorimeter proper.

5. This method is shown in several series of experiments to give a more constant result than the old method of calculation.

6. It is shown, moreover, to give essentially the same value for an adiabatic rise of temperature as that afforded by the old method when the latter is further corrected for the lag of the thermometer.

7. Therefore it appears probable that the true result of a calorimetric experiment can be attained only with the help of one or the other of these new methods, or some such method as that suggested by Richards and Lamb.